Environmental Pollution 241 (2018) 212–233

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Polycyclic Aromatic Hydrocarbons (PAHs) in inland aquatic ecosystems: Perils and remedies through biosensors and bioremediation☆

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ARTICLE INFO

Article history:
Received 13 February 2018
Received in revised form
24 April 2018
Accepted 4 May 2018

Keywords:
PAH
Aquatic ecosystem
Fish
Biosensor
Bioremediation

ABSTRACT

Polycyclic **A**romatic **H**ydrocarbons (**PAHs**) are among the most ubiquitous environmental pollutants of high global concern. PAHs belong to a diverse family of hydrocarbons with over one hundred compounds known, each containing at least two aromatic rings in their structure. Due to hydrophobic nature, PAHs tend to accumulate in the aquatic sediments, leading to bioaccumulation and elevated concentrations over time. In addition to their well-manifested mutagenic and carcinogenic effects in humans, they pose severe detrimental effects to aquatic life. The high eco-toxicity of PAHs has attracted a number of reviews, each dealing specifically with individual aspects of this global pollutant. However, efficient management of PAHs warrants a holistic approach that combines a thorough understanding of their physico-chemical properties, modes of environmental distribution and bioaccumulation, efficient detection, and bioremediation strategies. Currently, there is a lack of a comprehensive study that amalgamates all these aspects together. The current review, for the first time, overcomes this constraint, through providing a high level comprehensive understanding of the complexities faced during PAH management, while also recommending future directions through potentially viable solutions. Importantly, effective management of PAHs strongly relies upon reliable detection tools, which are currently non-existent, or at the very best inefficient, and therefore have a strong prospect of future development. Notably, the currently available biosensor technologies for PAH monitoring have not so far been compiled together, and therefore a significant focus of this article is on biosensor technologies that are critical for timely detection and efficient management of PAHs. This review is focussed on inland aquatic ecosystems with an emphasis on fish biodiversity, as fish remains a major source of food and livelihood for a large proportion of the global population. This thought provoking study is likely to instigate new collaborative approaches for protecting aquatic biodiversity from PAHs-induced eco-toxicity.

1. Introduction

Sustainability is not an option – it is a matter of how it is achieved. Degradation of the world's natural resources is rapidly outpacing the planet's ability to absorb the damage. This is primarily due to the extensive anthropogenic activities that along with unavoidable natural events have led to the deposition of a wide range of toxic compounds in the environment, turning this issue into an alarming global concern (Gianfreda and Rao, 2008). Today, one of

☆ This paper has been recommended for acceptance by Yong Sik Ok.

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https://doi.org/10.1016/j.envpol.2018.05.016
0269-7491/

the major environmental concerns in urban and industrial areas is **P**olycyclic **A**romatic **H**ydrocarbons (**PAHs**) as they pose a major threat towards global pollution. PAHs belong to the class of persistent organic hydrocarbons that consist of two or more fused aromatic rings (Fetzer, 2000; Igwe and Ukaogo, 2015; Sims and Overcash, 1983). One of the critical concerns with PAHs is their omnipresence in air, water, soil and aquatic sediments and high dwell time in the environment (Mrozik et al., 2003). Due to their high hydrophobicity, PAHs are difficult to be washed-off, and particularly in aquatic environments, they tend to get adsorbed on particulate matters and remain adsorbed for long periods. Among the hydrocarbon family of organic molecules, PAHs remain the most widely distributed toxic (Bamforth and Singleton, 2005; Samanta et al., 2002; Zhu et al., 2009), causing a number of adverse effects to aquatic organisms, including endocrine alteration (Meador et al., 2006), growth reduction (Christiansen and George, 1995), DNA damage (Caliani et al., 2009) and malformations of embryos and larvae (Carls et al., 2008). Fishes offer a good indicator of PAH pollution in water bodies (Nyarko and Klubi, 2011), as due to the high stability and lipophilicity of PAH (Bouloubassi et al., 2001), these get accumulated in fatty tissues of fish (Van der Oost et al., 1991) when ingested either through food (Meador et al., 1995) or through sorption *via* skin and gills (Gobas et al., 1999).

Fishes have been recognized as an important source of human protein diet, providing ~17% of the global intake of animal protein and 6.7% of all proteins (FAO, 2016). A large section of the human population depends on fisheries to meet their livelihood and nutritional requirements. However, with a significant increase in the anthropogenic activity in recent years, along with unavoidable process of biotransformation and biomagnification, the levels of PAH-based pollutants have become alarmingly high in the aquatic ecosystem (Nwaichi and Ntorgbo, 2016). The eventual consumption of these contaminated fishes has become an important pathway for human exposure to PAHs. Overall, thousands of PAHs are present in the environment but most of the studies remain focused on 16 priority pollutants (Yan et al., 2004) including potential human carcinogen, such as benzo[*a*]pyrene, chrysene, and benzo[*a*]anthracene (Andersson and Achten, 2015; Yan et al., 2004). For efficient environmental management of PAHs, it is important to co-consider multiple aspects in parallel, including their (i) distribution and eco-toxic effects, (ii) detection strategies, and (iii) potential remediation pathways. Considering the importance of PAHs, over the past decade, a number of reviews have been written on topics related to PAHs. The first category of reviews has focused on sources of PAHs in environments, their fate, and ecotoxic effects (Hamid et al., 2016; Hylland, 2006; Lawal, 2017; Meador et al., 1995). Another series of reviews has focused on potential remediation strategies for PAH-contaminated sites (Abdel-Shafy and Mansour, 2016; Haritash and Kaushik, 2009; Wilson and Jones, 1993). On the other hand, the current and potentially new detection strategies to identify PAHs have not yet been reviewed. Importantly, a review that consolidates all these PAH-related interdependent topics thereby providing a comprehensive understanding remains unavailable. Since the aquatic environment is the most critical contributor to the toxicity of PAHs, the current review focuses on critically analyzing the physico-chemical properties of PAHs, their source and distribution in aquifers, effect on aquatic organisms, existing approaches for their detection, and potential remediation strategies by employing catabolically diverse microbial community.

2. Physico-chemical properties of PAHs

The general characteristics of PAHs include high melting and boiling points, low vapor pressure, and poor water solubility (WHO, 1998). Individual PAHs vary in volatility and water solubility. The low molecular weight PAHs (two or three rings) are more easily degradable than those with higher molecular weights (four or more rings) due to relatively higher volatility and solubility of the former. Besides, the high molecular weight PAHs have the property to remain strongly fixated to soil sediments, thereby becoming resistant to microbial degradation. The incombustible nature of PAHs further keeps them persistent in the environment for long periods of time. PAHs are pollutants of high concern due to their toxic and growth/sex modulation effects not only towards aquatic organisms, but also in higher order animals and humans through bioaccumulation, leading to mutagenicity, carcinogenicity and genotoxicity (EC, 2002). The chemical structures of environmentally important PAHs are provided in Fig. 1 and their physico-chemical characteristics are enlisted in Table 1.

3. Environmental distribution of PAHs

3.1. Sources of PAHs in non-aquatic ecosystems

The last century of industrial development has caused a significant increase in PAHs concentrations in the environment (Wild and Jones, 1995). Three major sources of PAHs in the environments are pyrogenic, petrogenic and phytogenic (Fig. 2). In a pyrogenic process, PAHs are formed during pyrolysis where organic substances are burned at high temperatures ($\geq$350 °C) under low oxygen or anaerobic conditions. PAHs from pyrogenic activities are mostly found in urban areas (Abdel-Shafy and Mansour, 2016). Some of the largest sources of pyrogenic PAHs include the production of coke and coal tar during destructive distillation of coal, and the thermal conversion of crude petroleum into lighter hydrocarbon fractions (Enzminger and Ahlert, 1987; Guerin et al., 1977). Pyrogenic PAHs are also unintentionally formed during incomplete combustion of fuel in motor vehicles and power generators, and the woods during forest fires (Zou et al., 2003). In contrast, petrogenic PAHs are formed naturally during crude oil maturation over millions of years at low temperature (100–150 °C) (Abdel-Shafy and Mansour, 2016). These petrogenic PAHs get disseminated in the environment anthropogenically during transport, storage and use of crude oil and crude oil products (Stogiannidis and Laane, 2015). The major source of petrogenic PAHs in the ocean and fresh water are due to oil spills and storage tank leaks (Stogiannidis and Laane, 2015). Phytogenic (or more broadly biogenic) sources of PAHs include synthesis of such molecules by plants and lower order organisms such as bacteria and algae (Krauss et al., 2005). For instance, naphthalene, phenanthrene and their derivatives in plant wood of the Amazon basins were found to be accumulated in the termite nests (Wilcke et al., 2000). In fact, naphthalene concentrations in the plants and termite nests of tropical rainforest of Brazil were found to be as high as 1000 $\mu g\ kg^{-1}$ and 160 $\mu g\ kg^{-1}$, respectively (Krauss et al., 2005).

According to the World Health Organization, the smoke produced from combustion processes, such as in motor vehicles, from open fire places and tobacco consumption contains significant amounts of PAHs (WHO, 2010). It was estimated that worldwide 530,000 tons of 16 priority PAHs were emitted in the year 2004 alone, with China leading with 114,000 tons, followed by India with 90,000 tons, and the United States of America with 32,000 tons (Zhang and Tao, 2009). In coal processing plants, coal tar pitch is produced as a waste product. This coal tar loaded with hundreds of PAHs is widely used in road surfaces as a binding agent. Though in some developed countries, the awareness towards PAHs has led to the restricted use of tar; in many developing nations, it is still widely used in a number of products; for instance, for making water-proof roofs (Trumbore et al., 2015). High contents of PAHs have also been detected in consumer goods, such as in bicycles,